XXVIII.—*The Absorption Spectra of Diphenyl and Some Derivatives.*

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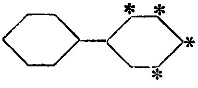
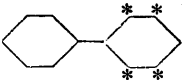
IN connexion with the relations between the constitution of organic compounds and their absorption spectra, it was shown (Baly, Edwards, and Stewart, J., 1908, **93**, 1902) that the seven-banded absorption spectrum of benzene can be explained by Collie's oscillation theory (J., 1897, **71**, 1013) for the structure of the benzene molecule on the assumption that each band corresponds to a make-and-break of valency. The spectrum of naphthalene was discussed in a similar manner (Baly and Tuck, J., 1906, **89**, 514) and found to be in agreement.

In the course of the following work, the resemblance manifest between the spectra of diphenyl and of its derivatives has led to a corresponding theory for this hydrocarbon. Since one carbon atom of each nucleus is bound, no valency oscillation involving only two carbon atoms can take place, nor is an oscillation involving all six carbon atoms possible. Three types of pulsation remain :


(I.)


(II.)

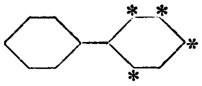
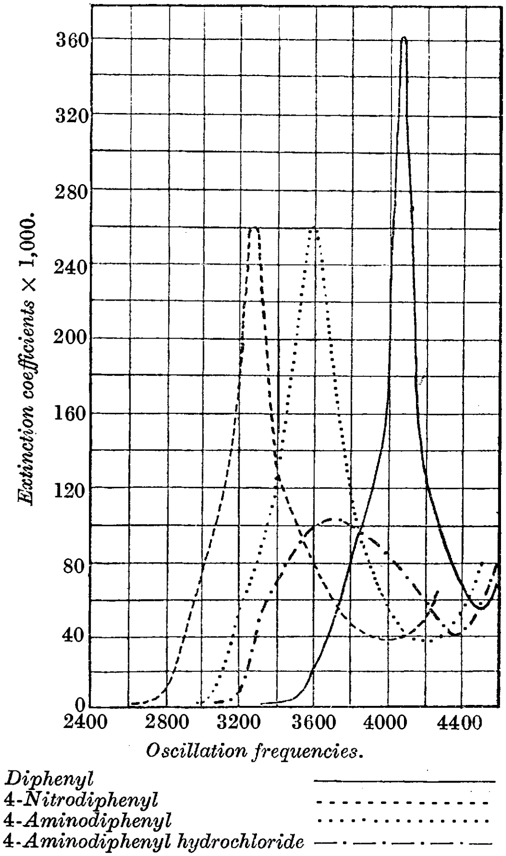

(III.)

Fig. 1.

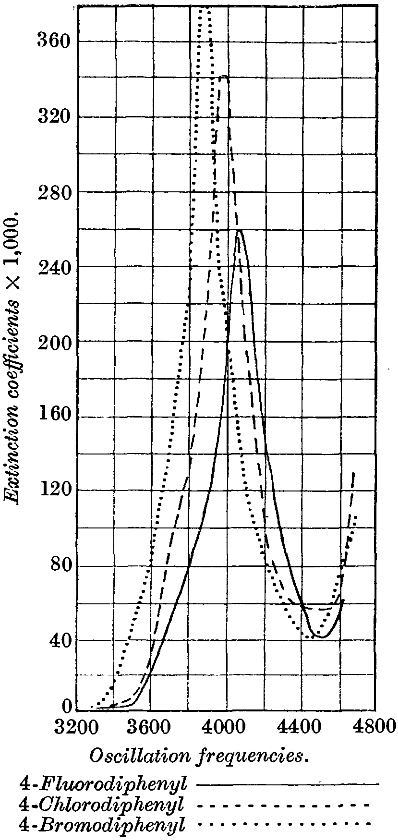


If the appearance of a band in the spectrum is to indicate a make-and-break of valency, then only one of these is possible. The same band is shown by the 4-derivatives as by diphenyl itself, an indication that the pulsation of the molecule does not include the carbon atom in the 4-position; that is, the oscillation of valency is taking place as in (II). The spectroscopic evidence thus points to the existence of a virtual para bond in the diphenyl molecule making the

4-carbon atom the stable member of the ring. The spectra obtained for the 2-derivatives bear out the theory in the following respects:

(1) The 4-carbon atom being partially bound by a virtual bond, any electronic disturbance which includes this atom will be small compared with the typical disturbance, and the resulting band will be absorbed in the typical band.

FIG. 2.



(2) If the main pulsation is suppressed by a 2-substituent, then selective absorption will be eliminated, except in so far as the 4-carbon atom is free to oscillate. In practice, 2-nitrodiphenyl shows one shallow band, and the heavily substituted 2-2″-diphenylyldiphenyl shows a band still shallower.

EXPERIMENTAL.

The solvent employed was, in most cases, spectroscopically pure ethyl alcohol. For 4-diphenylyldiphenyl and 4′-nitro-4-diphenylyldiphenyl, it was necessary to employ redistilled A. R. chloroform owing to the low solubility in alcohol.

The spectra were photographed with a Hilger Model 3 all-quartz ultra-violet spectrograph with rotating sector attachment. The persistence of the band is taken as being the difference between the extinction coefficients of the head of the band and of that frequency, towards the violet end, where complete transmission is obtained.

Diphenyl, m. p. 70·5°. The spectrum shows a deep well-defined band with its head at ν 4063 (see Fig. 1), in good agreement with the measurement of Baly and Tryhorn (J., 1915, **107**, 1058), who examined the spectrum of a thin film of diphenyl.

4-*Nitrodiphenyl*, m. p. 113°. Substitution of a nitro-group for hydrogen has moved the head of the band towards the red to ν 3259.

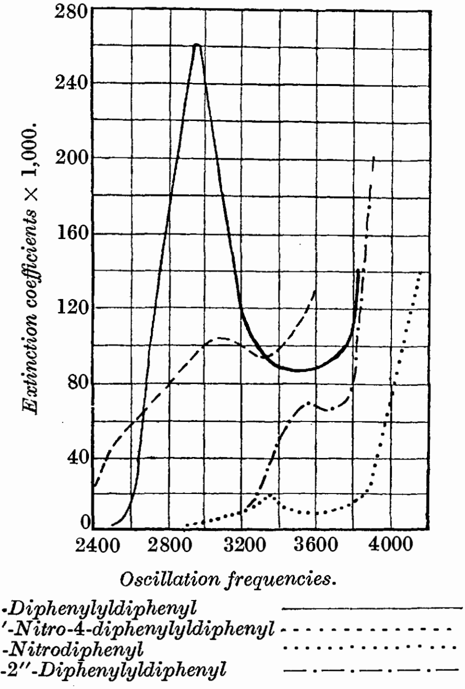
4-*Aminodiphenyl*, m. p. 53°. The amino-substituent has the effect of broadening the band. The size and mass of the group being less than in the previous instance, the band head has not been shifted to the same extent, maximum absorption occurring at ν 3590.

4-*Aminodiphenyl hydrochloride.* The reduction of reactivity consequent on the formation of the hydrochloride brings about a considerable decrease in the persistence of the absorption, in this case from 224 to 64 units. The head of the band has also moved back towards the ultra-violet to ν 3720.

4-*Fluorodiphenyl*, m.p. 74·5°. As might be expected, the entry into the diphenyl molecule of a small light atom such as fluorine has no appreciable effect on the absorption (see Fig. 2).

4-*Chlorodiphenyl*, m. p. 75·5°. In this case, the greater size and mass of the chlorine atom has shifted the position of maximum absorption to ν 3979. The band is also more persistent, although the configuration of the curve is unaltered.

FIG. 3.



4-*Bromodiphenyl*, m. p. 89°. Replacement of chlorine by bromine has the effect of moving the head of the band to ν 3892.

4-*Diphenylyldiphenyl*, m. p. 260°. Spectroscopically, at least, this compound acts as a heavily substituted diphenyl. The band, while retaining the characteristics of the diphenyl band, is shallower with a persistence of 172. The head has moved well up towards the red, occurring at ν 2965.

4′-*Nitro*-4-*diphenylyldiphenyl*, m. p. 274°. Although no definite band is shown, there is evidence of a very shallow band about ν 3050.

2-*Nitrodiphenyl*, m. p. 36°. The feeble valency oscillation permissible in a 2-substituted diphenyl is demonstrated in this case by the appearance of a very shallow band at ν 3350.

2-2''-*Diphenylyldiphenyl*, m. p. 185°. In conformity with the theory, the selective absorption shown by this compound is small, a very shallow band with its head at ν 3550 being obtained.

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